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Localized modes in biopolymers

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A formalism is developed using the FG-matrix technique due to Wilson for calculating the normal modes of vibrations of a homopolymer with a small percentage of impurity in it. It is shown, that, like in solid state physics, when the mass of the impurity is very different compared to that of the homopolymer, localized modes can appear. The frequencies due to these impurities lie in ranges forbidden to the normal modes of the perfect homopolymer. Resonance modes, whose frequencies lie in the range of frequencies allowed to the perfect homopolymer, and which are characterized by a large amplitude of vibration for the impurity, can also occur.

Since the localized modes are expected to occur in the far-infrared, and since the far-infrared region is associated with conformationally sensitive intra-chain bands and the less understood inter-chain interactions, it is felt that the impuriy techniques might prove as useful probes.

1. INTRODUCTION

Pioneering work by Lifshitz (1) showed that the normal modes of a perfect crystal could be drastically altered upon introduction of an impurity atom into it. This was a herald of what is now so popularly called as 'impurity physics'. In as much as homopolymers could be treated to a good approximation as single chains, they could be thought of as one-dimensional infinite crystals. Thus, when a substitutional impurity is present in a homopolymer, localized vibrational modes are expected to occur, with frequencies lying in ranges forbidden in the case of a homopolymer. There are some differences, though : since in the case of biopolymers, both the guest and the host have the same backbone, namely, -NH-CH-CO-, the only way of introducing impurities is through side groups, R. Since the changes in interactions are not going to be sufficiently different to lead to substantial changes in frequencies of homopolymers, the only way of bringing about effective changes seems to be by introducing side groups with masses very different from those of homopolymers. Outlined below is a formalism for computing the normal modes of a biopolymer with substitutional impurities.

2. Formalism

Consider a homopolymer without any defects, and characterized by mass M. An impurity, of mass m, where $M>>m$ (or $M<<m$), is substituted into the homopolymer. Since, it is our aim to study the properties of the host, it is necessary that the concentration of the guest be small enough not to change the host drastically and large enough to give rise to change in the host spectrum. This optimum concentration can be arrived at on empirical basis. It will be also assumed that the impurity is a point mass with no internal degrees of freedom, so that it does not affect the symmetry of the host. This is justified since the side groups—either in the host or guest—are usually treated as point masses devoid of internal degrees of freedom.

Thus, one can see that the chain continues to be periodic except at places where the guest is present. For the sake of simplicity, consider an isolated impurity at the chemical repeat unit $n=n'$. The case of multiple impurities could be tackled along similar lines. Let $H(\Psi, l)$ be the operation which transforms geometrically each repeat unit into the next. $H(\Psi, l)$ defines a rotation of Ψ about the chain axis and a translation of l along the same axis. By R^n_i we denote the i-th independent internal coordinate belonging to the n^{th} chemical unit. For small oscillations, the vibrational potential energy of the system

$$V = V(R_{in})$$

can be expanded, in the harmonic approximation, in a Taylor Series:

$$V = V_0 + \sum_{n,i} F_i^n R_i^n + \frac{1}{2} \sum_{n,m} \sum_{i,k} F^{nm}_{ik} R^n_i R^m_k ; \qquad (1)$$

with

$$F^n_i = \left(\frac{\delta V}{\delta R^n_i} \right)_0 \text{ and } F^{nm}_{ik} = \left(\frac{\delta^2 V}{\delta R^n_i \, \delta R^m_k} \right)_0 \qquad (2)$$

Assuming that the introduction of an impurity leaves the host in a stable condition, at the equilibrium configuration, $F^n_i = 0$. After shifting the zero to V_0,

$$2V = \sum_{n,m;i,k} F^{nm}_{ik} R^n_i R^m_k ; \qquad (3)$$

The expression for the kinetic energy can be obtained in a similar fashion In terms of the momenta P^n_i conjugated to the coordinates R^n_i and the kinetic energy matrix G, w have

$$2T = \sum_{n,m;i,k} G^{nm}{}_{ik} P^{n}_{i} P^{m}_{k}; \qquad (4)$$

Now we are in a position to discuss the effect of an isolated impurity at the repeat unit n=n′.

Force constants enter the secular equation through eq. (3) and the masses through eq. (4).

Case I : the mass of the impurity and the average interaction of the impurity with the host are the same as those of the host.

It is clear from eqs. (3) and (4) that the impurity spectra will be the same as those of the host and hence no new information is expected.

Case II : the mass of the impurity is very different from that of the host, but the interractions are essentially the same.

It is clear from eq. (4) that the expression for 2T will be

$$2T = \sum_{n;i,k} G^{nn'}{}_{ik} P^{n}_{i} P^{n'}_{k} + \sum_{\substack{n,m;i,k \\ (n,m \neq n')}} G^{nm}{}_{ik} P^{n}_{i} P^{m}_{k}; \qquad \ldots\ldots (5)$$

Thus, the solution of Euler-Lagrange equations can be written using eqs. (3) and (5). This leads to a system of an infinite number of second-order differential equations in the unknowns $R_i{}^{n'+s}$ whose solution can be assumed to be the plane wave :

$$R_i{}^{n'+s} = A_i \exp\,[-i(wt + s\delta)] \qquad \ldots\ldots\ldots (6)$$

In eq. (6), A_i is independent of n′, δ is the phase shift between two equivalent internal displacement coordinates in adjacent repeat units, and ω is the circular frequency. Substituting eq. (6) into the secular equation leads to a system of N simultaneous homogeneous linear equations in the unknowns A_i . Here N = 3r, r being the number of atoms in a repeat unit. The nontrivial solutions are

$$| G(\delta)\ F(\delta) - w^2\ (\delta)\ I | = 0, \qquad (7)$$

where

$$\begin{aligned} G(\delta) &= \sum_{i,k} G^{n'n'}_{ik} + \sum_{s=1}^{\infty} \left(G^{s} e^{is\delta} + \tilde{G}^{s} e^{-is\delta} \right) \\ F(\delta) &= \sum_{i,k} F^{n'n'}_{ik} + \sum_{s=1}^{\infty} \left(F^{s} e^{is\delta} + \tilde{F}^{s} e^{-is\delta} \right) \end{aligned} \qquad (8)$$

The maximum value of s, namely s_{max}, is that value of s for which the B matrix is nonzero. In the case of biopolymers, it is expected that $s_{max} = 3$. (*see below)

Eq. (7) is degree N in w^2. There are N roots $\omega^2 = 4\pi^2c^2\nu^2$ for each value of δ. Noting that $\nu(\delta) = \nu(-\delta)$ and $\nu(\delta+2\pi)=\nu(\delta)$ one can restrict oneself to the range $0 \leq \delta \leq \pi$. This corresponds to half of the first Brillouin Zone [2]. It might be mentioned in passing that the extent of coupling with neighbouring units through the G and/or F matrices decides the shape of the N frequency branches.

(*equations (8) show that it is possible, as in the case of solid state physics, to get both gap modes ($m << M$) and resonant modes ($m >> M$)).

3. Discussion

The formalism, outlined above indicates that it is, under certain conditions, possible to obtain localized modes whose peaks appear at places forbidden to a homopolymer. By introducing impurities of suitable mass, it is then possible to obtain frequencies which are so different from those of the host that they have no way to couple with those of the host. Thus, the modes die off very slowly and hence, through the principle of uncertainty, have very discrete energy. Lewis and Scheraga (3) studied the Laser Raman Spectra of random poly(hydroxybutylglutamine-CO-glycine) in the solid state. A band at 61 cm^{-1} and of width 1.2 cm^{-1} was interpreted by them as arising from specific effects of the incorporaaion of single glycyl residues in the helical sections of the copolymers. However, Shotts and Sievers (4) failed to observe this band by far-infrared techniques. Also, the width of the 61 cm^{-1} band is surprisingly small. Thus, the experimental reports are not only very inadequate but also controversial. Calculations on some specific systems, currently in progress in our Unit, are expected to throw some light on the situation.

In the meanwhile, there is need for more experimental work in this relatively virgin field. Inelastic neutron scattering techniques seem to be very useful, since the energy of thermal neutrons falls in the far infrared region. Impurity mode studies with Cl^- impurities with chlorine^{35} and chlorine^{37} isotopes have put the harmonic approximation into doubt (5). Similar doubts have been raised regarding the validity of the harmonic approximation by Macdonald (6) who attempt to fit the frequencies of localized modes due to hydride and deuteride impurities in KCl. These results in solid state physics have proved enigmatic, since one would think that in cases of isotopic substitution the force constants should be the same for the two isotopes. At this juncture, studies on impurity-doped homopolymers seem to be eminently needed.

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